# Micro-Scale Heterogeneity in Biogeochemical Uranium Cycling

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Abstract. One method for the *in situ* remediation of uranium contaminated subsurface environments is the removal of highly soluble U(VI) from groundwater by microbial reduction to the sparingly soluble U(IV) mineral uraninite. Success of this remediation strategy will, in part, be determined by the extent and products of microbial reduction. In heterogeneous subsurface environments, microbial processes will likely yield a combination of U(IV) and U(VI) phases distributed throughout the soil matrix. Here, we use a combination of bulk X-ray absorption spectroscopy (XAS) and micro-focused XAS and X-ray diffraction to determine uranium speciation and distribution with sediment from a pilot-scale uranium remediation project located in Oak Ridge, TN.

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## INTRODUCTION

One legacy of the Cold War is uranium contamination of surface water and groundwater at mining and nuclear processing sites throughout the United States. The mobility of uranium in the environment will in part be controlled by its oxidation state. In oxic groundwater, uranium is generally found in the hexavalent oxidation state and readily forms soluble complexes with carbonate, a common groundwater ligand. Conversely, U(IV) tends to be sparingly soluble and thus relatively immobile.

Numerous common, dissimilatory metal and sulfate reducing bacteria (DMRB and SRB, respectively) couple the oxidation of organic matter and $H_2$ to the reduction of U(VI), resulting in the precipitation of uraninite ($UO_2$) [1]. Thus, microbial U(VI) reduction may play an important role in the biogeochemical cycling, particularly in the natural attenuation of uranium. Current research is exploring the potential of *in situ* uranium remediation using native metal reducing bacterial populations stimulated by carbon addition [2].

For thirty-one years, trillions of gallons of acidic, uranium-bearing waste was generated at the Y-12 Facility, Oak Ridge, TN and discharged into the unlined S-3 Ponds, resulting in the contamination of groundwater. The U.S. Department of Energy has established a Field Research Center (FRC) adjacent to this former waste disposal site to asses the potential of *in situ* biological uranium reduction and precipitation as a means to limit uranium mobility in subsurface environments. After five years of operation, a pilot-scale system has reduced dissolved uranium concentrations several orders of magnitude through *in situ* biological uranium reduction [2]. Twenty-five to fifty percent of the solid-phase uranium in wells receiving ethanol was in the tetravalent oxidation state.

Given the complex chemistry of uranium in subsurface systems, it is important to determine not only its average oxidation state but also its micro-scale distribution. Here, we present a detailed analysis of sediment retrieved on October 5, 2005, from well FW102-3 in Area 3 of the FRC. We use bulk X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy to determine the bulk oxidation state and chemical speciation of uranium. We then complement these techniques with micro-focused XANES spectroscopy and X-ray diffraction (XRD) to show that reduced uranium is heterogeneously distributed throughout the

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sediment and that rutherfordine ($UO_2CO_3$) is one remnant U(VI) phase after eight months of sample aging.

## MATERIALS AND METHODS

### Site Description and Sediment Retrieval

Since August 2003, we have performed *in situ* biological uranium remediation experiments in the FRC Area 3, immediately adjacent to the former S-3 Ponds. Wu et al. [2] provides a detailed description of the field site and its operation to achieve the *in situ* biological uranium reduction.

The sediment was collected from well FW102-3 [2] then stored anaerobically at 4 °C until analysis. The bulk uranium oxidation state in a sample collected on October 5, 2005 (day 774) was examined both one month and eight months after collection. Micro-scale distribution and speciation of uranium was examined eight months after sample collection.

### Bulk X-ray Absorption Spectroscopy

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy were used to determine the oxidation state of uranium. Bulk XANES data was collected at beamline 11-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). Fluorescence spectra were recorded by monitoring the U $L_{III\alpha}$ with either a 13- (APS) or a 30- (SSRL) element Ge semiconductor detector. The energy range studied was -200 to +800 eV around the $L_{III\alpha}$-edge of U (17.166 keV).

XAS data were processed using the SixPACK [3] interface to IFEFFIT [4]. XANES data were background-subtracted and normalized to a unit-edge step. The relative amount of reduced uranium in samples was determined by comparison of the half height edge position of each sample to a standard curve obtained from samples with varying known mole ratios of U(IV)/U(VI). After background subtraction and normalization, the EXAFS data were extracted. Phase and amplitude functions for shell-by-shell fitting were generated using FEFF 7 [5] and the crystallographic atomic positions of rutherfordine. Models were fit to the data using the SixPACK interface to IFFEFFIT, which performs error analysis and calculates goodness-of-fit parameters.

### Solid-phase Micro-analysis

Synchrotron micro-X-ray fluorescence (μ–XRF) Mapping and micro-X-ray absorption spectroscopy (μ–XAS) and micro-X-ray diffraction (μ-XRD) measurements were performed on GSE-CARS beamline 13-ID-C at the Advanced Photon Source (APS, Argonne, IL). The incident X-ray beam was focused to a size of 2 x 2 μm using two Si mirrors in Kirkpatrick-Baez geometry. Sediments were mounted and analyzed as described in Ginder-Vogel et al. [6] .

Micro–XRD patterns were collected on select areas in transmission geometry using monochromatic radiation (20 keV) and a MAR 3450 image plate and analyzed as previously described [6].

## RESULTS AND DISCUSSION

The sediment samples retrieved from well 102-3 on October 5, 2005 were dark-green in color, indicative of reducing conditions, and contain 857 mg/kg uranium. The aqueous phase contained: sulfide, 11.4 mg/L; sulfate, 42 mg/L; and residual organic carbon electron donor, 85 mg/L as COD. XANES analysis of the sediments within one month of sample collection confirms uranium reduction, with 30% of the uranium present in the U(IV) state (Figure 1). Allowing the samples to age under anaerobic conditions, at 4 °C for eight months results in the accumulation of an additional 30% of reduced uranium (Figure 1).

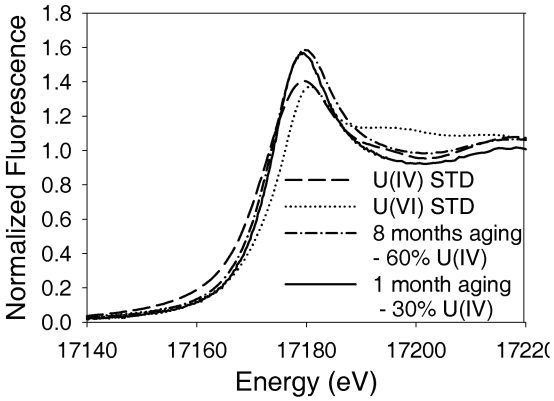


**FIGURE 1.** U $L_{III}$ XANES analyses confirming uranium reduction in sediment samples obtained on October 5, 2005. Samples were analyzed after one or eight months of aging.

The low coordination number (0.57) for the axial oxygen, obtained from analysis of the EXAFS spectra, confirms the presence of reduced uranium after eight months of aging (Figure 2). Furthermore, the EXAFS analysis reveals the presence of a split equatorial oxygen shell, with oxygen atoms present at 2.32 and 2.52 Å and a carbon atom at 2.93 Å (Figure 2), which may be indicative of a mixture of an uraninite-like phase and an U(VI)-carbonate phase. However, due to the lack of uranium-uranium scattering, it is not possible to further constrain solid-phase uranium speciation using EXAFS spectroscopy.

Synchrotron micro-X-ray fluorescence (μ-XRF) mapping of the uranium distribution reveals that uranium is present throughout the sediment. However, there are several spots, ranging from 50 to 100 μm in diameter, with approximately 3 times more uranium counts than the background (Figure 3). Uranium XANES analysis of these spots reveals that at least 90% of the uranium is present in the hexavalent oxidation state, while more U(IV) is present in areas of lower uranium concentration (data not shown). Micro-X-ray diffraction (μ-XRD) patterns collected from ten areas of high uranium concentration reveal the presence of quartz and rutherfordine ($UO_2CO_3$) (Figure 3). Micro-XRD patterns collected from areas of lower uranium concentration reveal solely the presence of quartz (data not shown). Interestingly, uraninite diffraction peaks were not observed—neither in areas of high nor low uranium concentration.

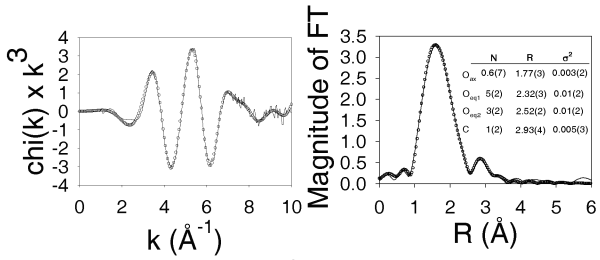


**FIGURE 2.** Averaged $\chi(k)\cdot k^3$ (left) and Fourier transform (right) of $\chi(k)\cdot k^3$ data (line) and fit (circles) from sample 102-3 after 8 months of aging. Data were fit simultaneously at k-weights of 1, 2 and 3 with a single $E_0$ of -3.5 eV from 0-4 Å, parameters derived from fitting are inset in the Fourier transform.

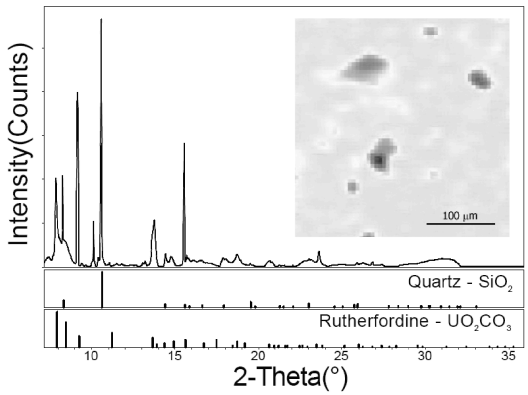


**FIGURE 3**. XRD pattern obtained from an area of high uranium(VI) concentration. Minerals identified in the pattern include quartz and rutherfordine. Inset; microanalysis of uranium distribution in sediment retrieved from well 102-3 and aged for 8 months. Darker colors indicate more U fluorescence, with white indicating ~ 1,000 counts per second and black indicating ~7,000 counts per second.

The success of biological uranium remediation will be determined, in part, by the extent of solid-phase uranium reduction. Initially, 30% of the solid-phase uranium is present in the U(IV) oxidation state. The proportion of reduced uranium increases to 60% with seven months of aging. Microanalysis of the sediment after aging reveals localized areas of predominantly U(VI), identified as rutherfordine using micro-XRD. Residual microbial activity due to the presence of residual electron donor and sulfate and elevated sulfide levels are likely responsible for the increase in U(IV). Additionally, it is likely that elevated carbonate concentrations in the aged sediments result in the precipitation of rutherfordine. Despite the presence of 60% U(IV) in the sample, uraninite is not detected using EXAFS spectroscopy or μ-XRD, likely due to the microcrystalline nature of biologically precipitated uraninite.

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